

VAPOR PHASE FORMATION OF NONCRYSTALLINE FILMS BY A MICROWAVE DISCHARGE TECHNIQUE

D. R. Secrist and J. D. Mackenzie

International Business Machines Corporation, Poughkeepsie,¹ New York
Rensselaer Polytechnic Institute, Troy, New York

ABSTRACT

Numerous variations of the microwave discharge method have been employed to prepare thin films. In this study, non-crystalline films were deposited at low temperatures and pressures by the vapor phase reaction of suitable compounds with the energetic gaseous species generated in a discharge operated at 2,450 megacycles/sec. The major part of the investigation concerned the decomposition of metal-organic compounds of the type $(R)_xM$ or $(RO)_xM$, where R may be C_2H_5 , C_3H_7 , etc. Amorphous oxide films of silicon, germanium, boron, tin, and titanium were readily formed when an oxygen plasma was maintained. Silica films were also grown via an argon plasma. These films were deposited on metallic and non-metallic substrates positioned outside the discharge region. Conversely, the oxidation of silicon tetrafluoride to yield a fluorsiloxane polymer of composition $SiO_{1.5}F$ was found to occur only within the confines of the plasma. It is shown that the films are free from decomposition products when deposited above a certain critical temperature, which is dependent on the reactant flow rate. The effects of temperature, pressure, flow rate, and hygroscopic nature of the substrate on the deposition rate are examined. Optical properties are presented. The utilization of a nitrogen or nitrogen oxide plasma to generate nitride or oxynitride films is discussed.

INTRODUCTION

Extensive studies have been conducted with crystalline films in regard to film structure, epitaxy, and property variations as a function of the history of a particular deposition process. The nature of glassy films, however, has not been investigated with the same thoroughness. This is due, in part, to the inability of most materials to form in the glassy state. In general, the approach to film formation has been from the vapor phase. Some methods from the vapor include evaporation, vapor phase hydrolysis, thermal decomposition, and "sputtering". All of these techniques will yield non-crystalline films with the proper conditions. However, with the exception of the latter method, relatively high temperatures are required. As a result, most films invariably crystallize immediately after being deposited. The non-crystalline films prepared by these techniques are usually materials which readily form a glass by the conventional cooling of a melt; e. g., SiO_2 . The method of sputtering, on the other hand, occasionally leads to the formation of uncommon non-crystalline films when the substrates are maintained at low temperatures⁽¹⁾. In this paper, the low temperature preparation of a wide variety of non-crystalline films is discussed utilizing a microwave discharge method as an alternative to sputtering. With this technique, the rate of film deposition can be carefully controlled by regulation of the reactant flow rates. The quality of any particular film is shown to be a sensitive function of (1) the concentration

and type of reaction products, (2) the chemical nature of the substrate, and (3) the reactor (substrate) temperature.

APPARATUS

A schematic drawing of the main flow system employed in this work is shown in Figure 1. A gaseous plasma, in this instance oxygen, could be maintained in a 1" O. D. pyrex tube when the system pressure was less than 800 microns. The electrodeless discharge was produced with a Raytheon PGM-10 Microwave Generator. This unit could supply 100 watts of microwave energy at a fixed frequency of 2,450 mc/sec. The energized species were allowed to flow into the bell jar through a 0.5" dia. pyrex tube. The metal-organic compounds selected for this work were liquids with a vapor pressure of about 0.5 mm. near-room temperature and were contained in a graduate cylinder immersed in a constant temperature bath. The metal-organic evaporation rate (flow rate) at any temperature could be altered by adjusting a 1 mm. dia. Teflon stopcock. The ultimate vacuum achieved in the system was 240 microns pressure with a gas flow rate of 176 cm³/minute. The majority of the studies were performed inside an aluminum furnace 2 1/4" in dia. x 4" long. A fused silica cylinder 1 3/8" in dia. x 2 1/2" long served as a second furnace core. The constant temperature zones for these furnaces extended one cm. above and below the gas inlet port with a maximum radial temperature variation of $\pm 5^{\circ}\text{C}$ for points one cm. from the cylinder axes. A fused silica balance having a sensitivity of 1 cm/mg. was employed to determine the rate of film deposition. Details of this apparatus have been previously reported⁽²⁾. In order to provide a secondary working geometry, the basic apparatus was modified as illustrated in Figure 2. This adaption was used to study the oxidation of silicon tetrafluoride.

FILM DEPOSITION AND EVALUATION

The substrates were positioned in the furnace reaction vessel with their wide dimension perpendicular to the gas inlet tube. The general cleaning procedure consisted of dipping the specimens into a 48% solution of hydrofluoric acid, followed by a rinse in distilled water. During the period when the furnace temperature was increasing the system was purged with the gas selected to form the plasma. In all work, the microwave generator was operated at 90% of its rated power output.

The films were deposited onto NaCl or KBr discs to facilitate examination by infrared transmission. Substrates of platinum, aluminum, Al₂O₃, and fused SiO₂ approximately one cm. in diameter were prepared for the rate studies. The index of refraction and isotropic character of film specimens obtained from the substrates and/or gas inlet tube were determined with a petrographic microscope. Debye-Scherrer x-ray diffraction powder patterns were made to establish whether the films were amorphous or crystalline.

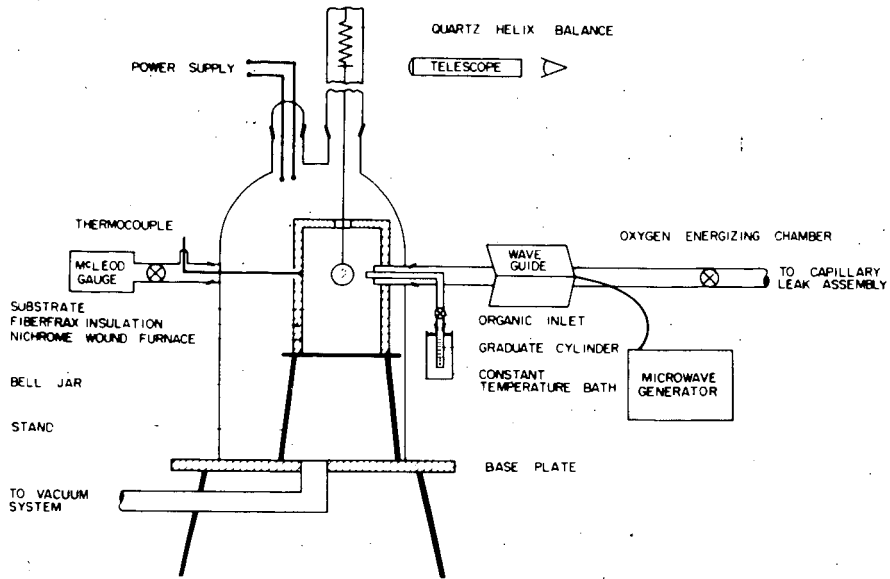


Figure 1: Schematic Drawing of Microwave Discharge Apparatus.

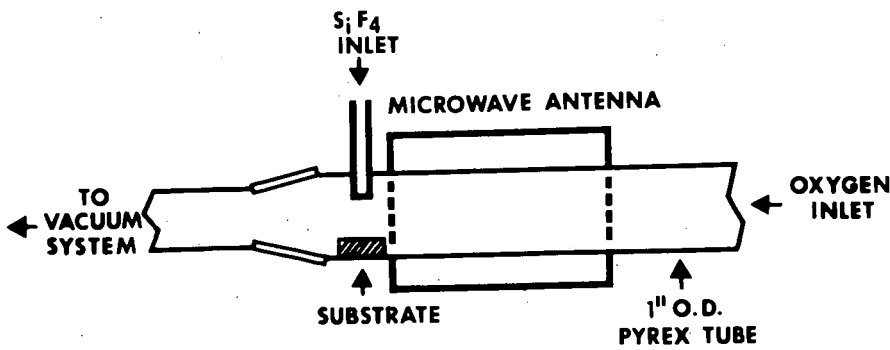


Figure 2: Modified Microwave Discharge System.

RESULTS AND DISCUSSION

Preliminary studies indicated that extensive water was formed as a reaction product when the metal-organic compounds were decomposed via an oxygen discharge. This water could be chemically incorporated into the oxide films when the substrates were held below a certain temperature which depended on the organic evaporation rate and the hygroscopic nature of the substrate. For instance, with NaCl substrates, the silica films were found to be free of water above 180°C with a tetraethoxysilane evaporation rate of 0.015 cm³/hour.⁽³⁾ The presence of silicic acid was detected below 180°C by infrared transmission studies. Conversely, with a KBr substrate and similar conditions of temperature and evaporation rate, extensive water was incorporated into the silica film.

The majority of the films prepared in this study were formed with low deposition rates of about 20 Å/minute on NaCl substrates heated to a temperature of 200°C. The optical properties of some of the films are presented in Table 1.

TABLE 1
COMPARISON OF THE OPTICAL PROPERTIES OF
VAPOR-FORMED FILMS AND THEIR RESPECTIVE
GLASSY OR CRYSTALLINE OXIDES

Material		Principal Infrared Frequency (CM ⁻¹)	Index of Refraction
SiO ₂ :	vapor-formed film	1,045;800	1.458+ .002
	fusion-formed glass	1,080;800	1.458+ .002
GeO ₂ :	vapor-formed film	850	1.582+ .002
	fusion-formed glass	860	1.534-1.607
B ₂ O ₃ :	vapor-formed film	1,350	1.470+ .002
	fusion-formed glass	1,370	1.464 ⁽⁴⁾
Ti _x O _y :	vapor-formed film	950-700	>1.7
TiO ₂ :	anatase	1,200-500	>1.7
Sn _x O _y :	vapor-formed film	1,425	1.536+ .002
SnO ₂ :	cassiterite	850-500	>1.7

All of the films were isotropic when examined with polarized light and were amorphous by x-ray diffraction. The silica films were formed by (1) decomposing tetraethoxysilane, (C₂H₅O)₄ Si, in either an oxygen or argon plasma or (2) decomposing tetraethoxysilane in an oxygen plasma. The germania and boron oxide films were prepared by decomposing tetraethoxygermane and triethylborate via an oxygen discharge. The infrared absorption frequencies and refractive indices of the latter three vapor-formed films are similar to those of the respective fusion-formed glasses, which suggests that a random network structure can be achieved by methods other than the conventional cooling of the melt. The spread in the index of refraction for germania glass was realized by slowing cooling one specimen and quenching another from 1100°C; the slow-cooled specimen had the larger refractive index. With the exception

of the boron oxide film, the films listed in Table 1 adhered well to the NaCl substrates. The B_2O_3 film was immediately coated with mineral oil after removal from the glow discharge apparatus because of its extreme moisture sensitivity and was only partially adherent.

The non-crystalline titanium oxide films were prepared from titanium tetra-isopropylate while maintaining an oxygen discharge. Since titanium oxide is not a common glass-forming system, one may inquire as to whether or not the viscosity of such a film would be similar to that of a glass near its transition region, e. i. 10^{13} - 10^{14} poises. For many undercooled systems, the growth rate can be described in terms of the reciprocal viscosity⁽⁵⁾ as:

$$u = \frac{\Delta H_f (T_f - T)}{3 T_f \pi \lambda^2 \eta N}$$

where u is the rate of growth (cm/sec), T is the undercooled temperature, η is the viscosity (poises), T_f is the fusion temperature, λ is the mean jump distance (cm), H_f is the latent heat of fusion (ergs), and N is Avogadro's number. If this relationship is valid for a system, then an approximate estimation of the viscosity at the crystallization temperature can be made if the rate of growth (crystallization) is known. In this study, the titanium oxide film exhibited birefringence (crystallized) after 45 minutes at 325°C . An approximate rate of crystallization can be calculated for the film if it is assumed that the particles grew from some arbitrary value, for example, 10 \AA to 110 \AA , before crystallinity was detected. The jump distance λ was taken as 2 \AA units. Although TiO_2 dissociates, the heat of fusion has been reported as 15.5 kcal/mole at a melting point of 1840°C ⁽⁶⁾. The growth rate determined from the rate of crystallization is about $3.7 \times 10^{-10} \text{ cm/sec}$. The corresponding viscosity at 598°K is 5.5×10^{11} poises, which would classify the film as a highly viscous supercooled liquid since the viscosity value is slightly below 10^{13} - 10^{14} poises. Since viscosity is approximately an exponential function of temperature, it is reasonable to conclude that at some slightly lower temperature the viscosity of the film is characteristic of a solid glass, e. i. 10^{13} - 10^{14} poises.

An amorphous tin oxide film was formed by decomposing dibutyltin-diacetate via an oxygen plasma. Preliminary measurements indicated that the electrical resistivity of the film near room temperature was greater than 10^7 ohm-cm . Comparing the I. R. spectra of the film and SnO_2 , it is seen in Table 1 that the main absorption mode for the amorphous film occurs at a much higher frequency than that of the crystalline modification. This shift can probably be attributed to a large structural variation such as a change in coordination number.

The basic apparatus shown in Figure 1 was modified as illustrated in Figure 2 in order to study the oxidation of SiF_4 via an oxygen discharge. Research grade SiF_4 gas was metered into the pyrex chamber at a rate of $1.8 \text{ cm}^3/\text{minute}$. Simultaneously, dry oxygen was admitted at the rate of $5 \text{ cm}^3/\text{minute}$. The electrodeless discharge was maintained at 800 u total pressure. Under these conditions, a thick non-adherent film was deposited onto the walls of the pyrex

chamber within the boundaries of the plasma in about one hour. The wall temperature in this region was approximately 100°C . The film can be described as a translucent blue-white gel which was amorphous by x-ray diffraction and isotropic when observed with polarized light. The index of refraction of the gel was estimated to be considerably less than 1.400; infrared absorption bands were evidenced at 1080, 920, and 750 cm^{-1} . A microchemical analysis of the film indicated that its composition could be represented as $(\text{SiO}_{1.5}\text{F})_n$. It is interesting to note that the film formed only within the confines of the plasma, which suggests that thermal and/or microwave energy are required for the oxidation and/or polymerization processes.

Effect of Pressure, Temperature, and Substrate - An extensive study was made with the silica films with respect to the mechanism and kinetics of film formation⁽²⁾. It is reasonable to suspect that the general conclusions formulated in this work with respect to pressure, temperature, and nature of the substrate are applicable to most of the other oxide films discussed in this manuscript. Support for this viewpoint is also documented in regards to the incorporation of water into the films⁽³⁾.

Basically, the effect of minor pressure fluctuations on the rate of deposition of silica films was found to be negligible. However, above 500 microns pressure, the rate of deposition was rapidly decreased due to (1) an increased atomic oxygen recombination and (2) poisoning effects from the reaction products. The films discussed in the present work were deposited near 240 μ pressure. Typical rates of deposition for the silica films ranged from 10 to 80 $\text{\AA}/\text{min}$. by variation of (1) the organic evaporation rate or (2) the substrate temperature. The rate of deposition was constant with time. The relationship between logarithm of the deposition rate and reciprocal temperature is depicted in Figure 3 for various substrates. The data have been spread to show the temperature dependence of deposition with each substrate. With a tetraethoxysilane evaporation rate of $0.15\text{ cm}^3/\text{hour}$, the silica films were free of water and/or organic inclusions (by infrared transmission studies) above $\sim 290^{\circ}\text{C}$. At higher temperatures, the rate of deposition decreased with increasing temperature and was ascribed to a process of physical adsorption. The apparent heat of adsorption of silica glass on the fused silica, NaCl, and platinum substrates was calculated to be $12.7 \pm 0.2\text{ kcal/mole}$. For the aluminum or Al_2O_3 substrates, the apparent heat of adsorption of silica was calculated to be $9.5 \pm 0.3\text{ kcal/mole}$. It was concluded that the hygroscopic nature of the Al_2O_3 surface was responsible for the lower heat of adsorption observed. It was postulated that a hydrated surface tends to incorporate further hydroxyl groups into the film structure. With this reasoning, one might expect that the hygroscopic nature of the KBr substrate discussed earlier would also lead to a decreased heat of adsorption. In conclusion, it is postulated that the rate of deposition of an oxide film with a moisture sensitivity similar to that of silica is most likely affected in the same manner, e. i. physical adsorption controlled below 410°C . The apparent heat of adsorption of the oxide films on the various substrates, is of course, dependent on the molecular structure of the films and the hygroscopic nature of the substrate.

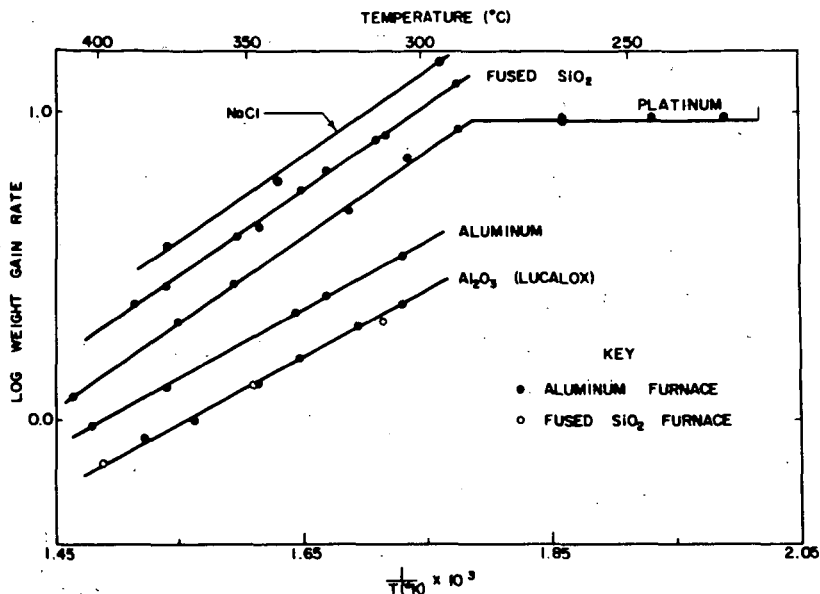


Figure 3: Relationship of Logarithm Silica Deposition Rate and Reciprocal Temperature for Deposition on Various Substrates.

Other Systems - The microwave discharge technique can be employed to deposit a variety of thin films at low temperatures. One obvious variation of the technique utilizes gaseous plasmas other than oxygen. For instance, in the work with silica films it was found that $(C_2H_5O)_4Si$ contained sufficient oxygen to facilitate the formation of SiO_2 when the compound was decomposed with energetic argon species. Sterling and Swann⁽⁷⁾ have recently deposited amorphous Si_3N_4 films by the reaction of silane and anhydrous ammonia in an RF discharge. Non-crystalline silicon nitride films have also been prepared at Rensselaer Polytechnic Institute by the decomposition of $(C_2H_5)_4Si$ via a nitrogen discharge. The use of a N_2O plasma to form Si_2ON_2 poses another equally interesting possibility. Success to date with the latter reactions has been complicated by the ease of formation of silica. Since metal-organic compounds are now available for a large number of metals, it would seem that the microwave discharge technique could lead to many new and unusual films by a simple variation of the reactant and/or plasma compositions.

References

1. R. A. Mickelson, "Electrical and Optical Properties of Amorphous Zinc Oxide Films", Sc. D. Thesis, M. I. T., 1963.
2. D. R. Secrist and J. D. Mackenzie, "Deposition of Silica Films by the Glow Discharge Technique", J. Electrochem. Soc. 113 (9), 914-920, (1966).
3. D. R. Secrist and J. D. Mackenzie, "Incorporation of Water Into Vapor Deposited Oxide Films", Solid State Electronics, 9, 180 (1966).
4. G. W. Morey, "The Properties of Glass", 2nd Edition, Chap. XVI, p. 370, Reinhold Publishing Corp., New York, 1954.
5. David Turnbull, p. 225 in Solid State Physics, Vol. 3, edited by F. Seitz & D. Turnbull, Academic Press, Inc., N. Y. 1956.
6. Q. Kubachewski and E. Evans, Metallurgical Thermodynamics, p. 306, Pergamon Press, N. Y. 1958.
7. H. F. Sterling and R. C. G. Swann, "Chemical Vapor Deposition Promoted by R. F. Discharge", Solid State Electronics 8, (8) p. 653-54 (1965).

Acknowledgements

The authors are grateful to the Pittsburgh Plate Glass Company for the support of a fellowship. (D. R. S.).